FUEL PROCESSING REQUIREMENTS AND TECHNIQUES
FOR FUEL CELL PROPULSION POWER

by

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ABSTRACT

Fuels for fuel cells in transportation systems are likely to be methanol, natural gas, hydrogen, propane, or ethanol. Fuels other than hydrogen will need to be reformed to hydrogen on-board the vehicle. The fuel reformer must meet stringent requirements for weight and volume, product quality, and transient operation. It must be compact and lightweight, must produce low levels of CO and other byproducts, and must have rapid start-up and good dynamic response. Catalytic steam reforming, catalytic or non-catalytic partial oxidation reforming, or some combination of these processes may be used. This paper discusses salient features of the different kinds of reformers and describes the catalysts and processes being examined for the oxidation reforming of methanol and the steam reforming of ethanol. Effective catalysts and reaction conditions for the former have been identified; promising catalysts and reaction conditions for the latter are being investigated.

INTRODUCTION

Electric vehicles powered by fuel cells require hydrogen as the fuel. This can be obtained directly from onboard pressurized cylinders. For example, Ballard Power Systems, Inc., will be unveiling a 9.75 m (32-ft.), 20 passenger bus later this year in Vancouver, British Columbia. This bus will be powered by a 100 kW polymer electrolyte fuel cell (PEFC), with hydrogen stored as compressed gas at 20.7 MPa (3000 psi). The driving range will be limited to 161 km (100 miles).

On a commercial level, the logistics of hydrogen supply to refueling stations, the mechanism of cylinder exchange or refueling at the stations, the driving range (i.e., the time/distance required between refueling), the weight penalty imposed due to a bulky and heavy cylinder, and the safety concerns of carrying a cylinder of hydrogen have led to a search for alternative hydrogen storage systems or alternative fuels from which hydrogen can be produced onboard.

Hydrogen can also be stored as a metal hydride or as an adsorbed gas on activated carbon. These methods require a large weight and volume per unit of hydrogen stored. Consequently, the amount of hydrogen that can be stored onboard is limited. In turn, the driving range of the vehicle is limited. Reforming of liquid fuels provides a viable alternative to on-board hydrogen storage. These fuels would preferably be liquids or capable of being liquefied at moderate to low pressures, can easily be made available at the refueling stations, and possess a high hydrogen/carbon ratio.

Of the different fuels being considered for use in fuel-cell powered vehicles, methanol has clear advantages in terms of fuel storage and distribution as it can be used with minimal disruption to the present fuel distribution network.[1,2] Methanol is a commodity chemical; it can be manufactured from coal, natural gas, or other feedstocks; and can easily be reformed to hydrogen at low temperatures. Ethanol, another alternative, is a renewable energy source produced from corn or other biomass and has 30% more energy than an equal amount of methanol.

The fuel cell powered bus program, sponsored jointly by the Departments of Energy and Transportation (DOE/DOT) is planning to field test prototype buses. These 8.8-m (29-ft) long, 20-27 passenger buses will be powered by a battery combined with a phosphoric acid fuel cell. Liquid methanol will be reformed onboard to provide the hydrogen for the fuel cell.

An on-board fuel processor has to meet a number of restrictions unique to transportation applications. The fuel processor needs to be compact and lightweight, since the vehicles have limited space and the total vehicle weight determines the power requirements and thus the "engine" size. Depending on the type of fuel cell that receives the hydrogen-rich reformate, the quality of the reformate can be very important. For example, polymer electrolyte fuel cells (PEFC) are very sensitive to the levels of carbon monoxide in the reformate and contaminants such as formic acid, acetic acid, acetaldehyde.

On-board fuel processors need a rapid start-up capability, i.e., they should be able to warm up to reaction conditions and deliver the required hydrogen to the fuel cell very quickly. Non-steady state operation (acceleration, braking) being an integral part of transportation power requirements, the fuel processor must be responsive to changes in hydrogen demand and have a high turndown ratio (idling).

If the fuel processor is designed around a catalytic reformer, the above-mentioned constraints translate, in terms of the catalyst, to the following. The catalyst should be very active to achieve a compact, lightweight reactor; give good product selectivity to obtain high hydrogen fractions as well as minimize reformate cleanup; and operate at relatively low temperatures to enable rapid heatup to reaction conditions. In addition, the catalyst should be rugged – capable of withstanding the vibrations; should have a long life – not requiring frequent regeneration or recharging; and should possess good thermal properties – high thermal conductivity to avoid hot/cold spots and resistance to sintering. As always, the material cost and availability are important issues as well.
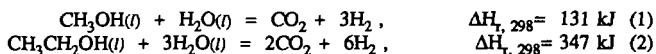
REFORMING AND REFORMERS

Fuel reformers are commonly used in chemical process industries for the manufacture of hydrogen from common feedstocks such as natural gas, propane, butane, and naphtha. The two most commonly used processes are (1) steam reforming and (2) partial oxidation in the presence of steam. Catalysts for the steam reforming process have already been demonstrated for methanol[3] and methane.[4]

Fuel reformers for the production of hydrogen for use in fuel cells have been developed more recently. Much of this development work, however, has concentrated on stationary applications, with essentially constant system load and process throughput. Reformers have been built and tested for converting methanol and natural gas to a hydrogen-rich fuel gas. Reforming of a variety of others fuels, including gasoline, diesel, and naphtha, has also been demonstrated. For constant-load stationary applications, steam reforming is preferred over partial oxidation reforming, since the former provides a higher overall

system efficiency as well as a reformate with a higher hydrogen concentration. Steam reforming is endothermic and requires the input of thermal energy.
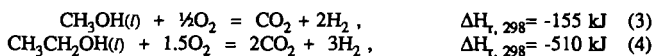
Methanol steam reforming is a well-studied reaction. The reaction stoichiometries for the steam reforming of methanol and ethanol are shown in Equations (1) and (2). Both reactions are endothermic.

$$CH_3OH(l) + H_2O(l) = CO_2 + 3H_2 , \qquad \Delta H_{r, 298} = 131 \text{ kJ} \quad (1)$$
$$CH_3CH_2OH(l) + 3H_2O(l) = 2CO_2 + 6H_2 , \qquad \Delta H_{r, 298} = 347 \text{ kJ} \quad (2)$$

Commercial catalysts can catalyze reaction (1) at relatively low temperatures (150°-250°C) with good selectivity. The catalysts are sufficiently active that the reformer designs are not limited by the reaction rate, but by the rate at which the heat for the endothermic reaction can be provided. Not surprisingly then, the reformer designs are more akin to heat exchangers than to conventional catalytic reactors. Several manufacturers have come up with various designs that look like shell-and-tube (Engelhard Corp.[5]) and plate-and-frame (Ishikawajima-Harima Heavy Industries[6]) heat exchangers. The packed-bed reformer built under the joint General Motors-Allison/Los Alamos National Laboratory[7] program uses an electric heater and gas recycling to maintain the desired bed temperatures. The presence of the recycle stream also serves as a surge tank to meet limited transient needs.

At present, effective catalysts or reformers have not been demonstrated for the steam reforming of ethanol.

The reactions for partial oxidation reforming are exothermic, and the reaction stoichiometries for methanol and ethanol are shown in Equations (3) and (4).

$$CH_3OH(l) + \tfrac{1}{2}O_2 = CO_2 + 2H_2 , \qquad \Delta H_{r, 298} = -155 \text{ kJ} \quad (3)$$
$$CH_3CH_2OH(l) + 1.5O_2 = 2CO_2 + 3H_2 , \qquad \Delta H_{r, 298} = -510 \text{ kJ} \quad (4)$$

Although a good partial oxidation reforming catalyst has been found at Argonne, the same cannot be said for the partial oxidation reforming of ethanol. Testing of the methanol partial oxidation catalyst and the search for an ethanol partial oxidation catalyst are continuing.

For transportation applications, the partial oxidation reformer can be much superior to the steam reformer with respect to its start-up and load-following performance.[1] For example, during start-up the reaction, once ignited, generates its own heat and thus can heat up the catalyst bed within a very short time. In contrast, the steam reforming catalyst bed receives the heat from across a surface. Similarly, at times of acceleration, the partial oxidation reformer merely requires additional feed, whereas the steam reformer requires both additional feed and heat, the latter being supplied across a boundary.

The partial oxidation reformer, using air for the oxidation process, produces a reformate that contains nitrogen, which reduces the hydrogen concentration in the reformate stream. In comparison, the steam reformer can, theoretically, provide up to 75% hydrogen in the reformate stream.

CATALYSTS FOR PARTIAL OXIDATION OF METHANOL

A number of catalysts for the partial oxidation of methanol have been studied in the laboratory. The tests consisted of methanol and water vapors fed in with a helium stream, mixed with oxygen, and passed

over a catalyst bed (~0.5 g) at temperatures of 150-400°C. The product stream was analyzed with a gas chromatograph.

Table 1 shows the product distributions obtained with some of these materials. Column 1 (methanol) shows that the Co/SiO$_2$ gives the highest (100%) conversion, but the hydrogen fraction is quite low at 24%; most of the hydrogen produced is oxidized to water (52%), which is undesirable. The CuZnO gives the highest hydrogen fraction; its overall conversion is very good, with only 1.6% methanol in the product stream; and this catalyst produces no methane. Although some CO is produced, if necessary, it can be converted via the water-gas shift reaction at low temperatures. Of the materials tested, the CuZnO catalyst appears to be the best choice in terms of activity and selectivity.

Table 1. Methanol Partial Oxidation Products Obtained with Different Materials

Catalyst	CH$_3$OH vol.%	H$_2$O vol.%	CO$_2$ vol %	H$_2$ vol.%	CO vol.%	CH$_4$ vol.%	Others vol.%
Pd/SiO$_2$	10.2	55	14	15	1.9	0.04	3.2
CuZnO	1.6	37	21	40	1.1	0	0
CuBiO/SiO$_2$	9.8	76	11	2	0.2	0	1.1
FeZnO	10	52	15	22	0.7	0.4	0
Co/SiO$_2$	0	52	18	24	0.5	5.1	0

Figure 1 shows the methanol conversion and hydrogen selectivity obtained with CuZnO as a function of temperature. Starting at a conversion of 70% at 275°C, the conversion increases and reaches nearly 98% at 325°C. At 400°C, all of the methanol gets converted. The level of hydrogen in the product stream remains almost unchanged at 63% throughout the temperature range. The maximum hydrogen mole percent achievable, as indicated from the reaction stoichiometry, is 67%. The figure also shows the levels of carbon monoxide, which is an undesirable product for low temperature fuel cells, such as the PEFC. The carbon monoxide does increase with temperature, but even at 400°C, it is a moderate 2%. Further testing of this catalyst in a bench-scale reformer is in progress.

CATALYSTS FOR STEAM REFORMING OF ETHANOL

A number of nickel-based catalysts have been studied in a reactor loaded with ~2 g of catalyst at temperatures of 250-450°C and fed a mixture containing 20 mol % ethanol (80 mol % water). The product gases were analyzed for hydrogen, carbon monoxide, carbon dioxide, and methane. A gas chromatograph was used for this analysis. The conversions were estimated from the product gas flow rates, ranging from 20 to 55%. Figure 2 shows the distributions in the gaseous product obtained with one of these catalysts as a function of temperature. At 250°C, the gaseous product was predominantly hydrogen (56%), carbon monoxide (23%), and methane (25%). With increasing temperature the CO fraction dropped sharply and was accompanied by increased fractions of carbon dioxide and methane. At ~400°C, the H$_2$ and CH$_4$ fractions passed through a minimum and maximum, respectively. Above 400°C, the CO$_2$ was found to level off, the CO and H$_2$ started to increase, while the methane fell off sharply to under 25%. The products also contained some acetaldehyde and acetic acid. The catalyst was found to deactivate due to coke deposition.

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This product distribution suggests a reaction mechanism involving dehydrogenation of ethanol, followed by dissociation of acetaldehyde to form methane and carbon monoxide. The decreasing levels of carbon monoxide indicate some conversion via the water-gas shift reaction. This is consistent with other studies[8] with nickel, where ethanol was found to undergo dissociation, leading all the way to coke deposition. Some other formulations showed lower conversions and higher levels of carbon monoxide.

The presence of methane in the product stream represents a loss in hydrogen-producing capacity, because the reforming of methane requires temperatures higher than 700°C. Other materials and formulations which will catalyze mechanisms offering better product selectivity are being investigated .

CONCLUSIONS

Fuel cells for transportation applications offer some choices and impose some unique restrictions upon the fuel processor. The choice of fuel, the weight/volume limitations, the rapid startup and transient response requirements, the need for durability in a mobile environment, and the overall efficiency of the fuel cell system are important considerations in the design of the fuel processor.

Methanol and ethanol have the potential to be the fuel of choice, provided the reforming processes can be demonstrated within the boundaries of the application requirements. Catalytic partial oxidation of methanol can provide the rapid startup and dynamic performance demanded in transportation applications, and a copper-zinc oxide catalyst is capable of supporting such a reformer.

Alternative reformer designs are being evaluated, and the catalyst screening continues for the steam reforming and partial oxidation reforming of ethanol.

ACKNOWLEDGEMENTS

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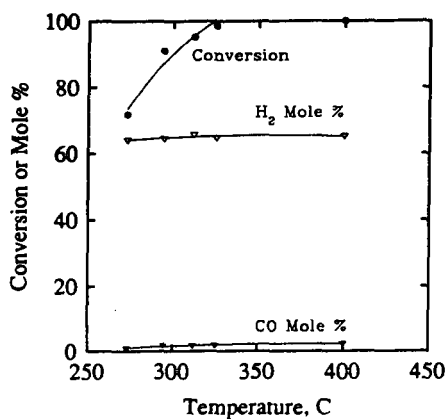   (1986).

Fig. 1. Methanol conversion and mole percent
         of hydrogen and carbon monoxide
         obtained form partial oxidation of
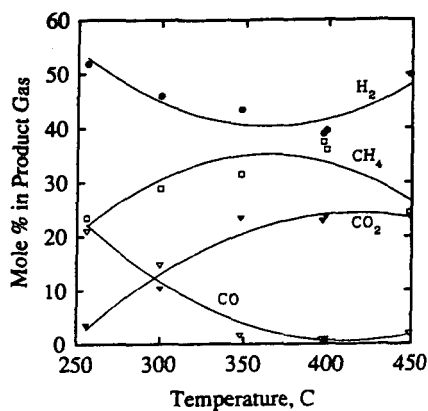   methanol over CuZnO.

Fig. 2 Product gas distributions
        obtained with ethanol and
        over a nickel-based